

# Nitrogen chemisorbed layers on GaAs(100): formation, properties, applications

V. L. Berkovits<sup>†</sup>, V. P. Ulin<sup>†</sup>, T. V. L'vova<sup>†</sup> and Akira Izumi<sup>‡</sup>

<sup>†</sup> Ioffe Physico-Technical Institute, St Petersburg, Russia

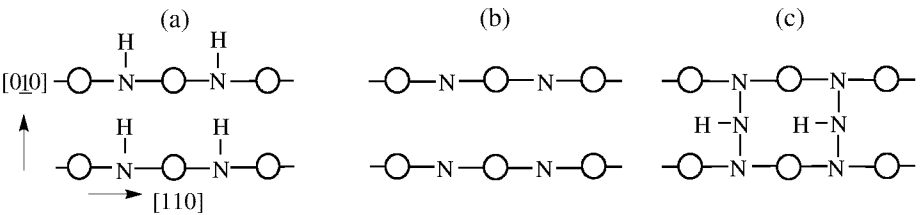
<sup>‡</sup> Japan Advanced Institute of Science and Technology,  
Tatsunokuchi, Ishikawa 923-1292, Japan

**Abstract.** We propose a novel wet chemical technology to form continuous nitride films on GaAs (100). For this nitridation hydrazine ( $N_2H_4$ )-based water solutions are used. X-ray photoemission analysis has shown that on the nitridized surfaces Ga-N surface bonds are dominant. We demonstrate that the proposed nitridation improves electronic properties of GaAs(100) and produce an effective surface chemical passivation.

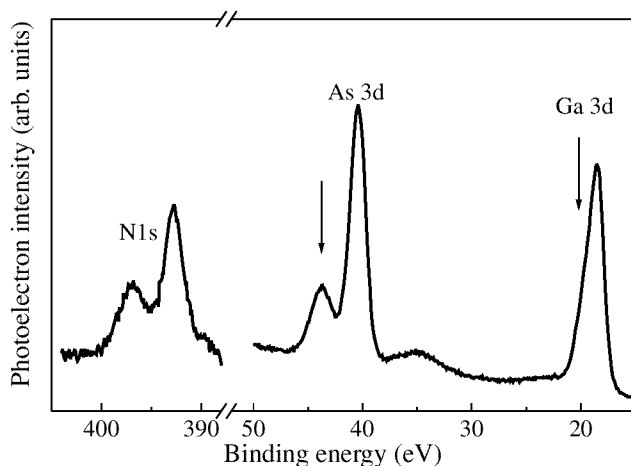
Nitridation of GaAs(100) is known to be a promising way of electronic and chemical surface passivation and also to be a crucial step for epitaxial growth of cubic GaN. However, existing methods of nitridation based on high-temperature treatment of the crystal in atmosphere of nitrogen precursors such as  $NH_3$ , hydrazine-related compounds, or  $N_2$  plasma lead to formation of relatively thick, amorphous or defect crystalline GaN-layers [1, 2].

Here we demonstrate that nitridation of GaAs(100) can be successfully performed by a wet chemical treatment of the crystal in alkaline hydrazine ( $N_2H_4$ )-based water solutions. The chemistry of this treatment includes the following stages: (i) removal of the natural oxide layer in the alkaline ambient, (ii) formation of the electrophilic adsorption centres on the crystal surface through electron transfer from semiconductor to  $H_3O^+$  or  $N_2H_5^+$  cations of the solution, (iii) removal of the surface arsenic atoms and uncovering of Ga-terminated (100) surface, (iv) dissociative adsorption of the hidrazine molecules on the Ga-related centres.

The dissociative adsorption of hydrazine is believed to proceed through several successive stages. At the initial stage one of the nitrogen atoms of hydrazine molecule forms chemical bonds with two neighbouring Ga- atoms in a bridge-site position. At the same time two protons pass into the solution. Shown in Fig. 1 final atomic configurations of nitridized (100) GaAs are allowed to be formed through the pair interactions between the hydrazine admolecules or through their interaction with  $H_2O$ . (i) The hydrazine admolecules can interact with  $H_2O$  producing chemisorbed NH groups on the surfaces and  $NH_2OH$  molecules



**Fig. 1.** Allowed atomic configurations of nitridized GaAs(100) (top view).



**Fig. 2.** XPS spectra of N(1s), As(3d) and Ga(3d) from chemically nitridized GaAs. Positions of the chemically shifted components are indicated by arrows.

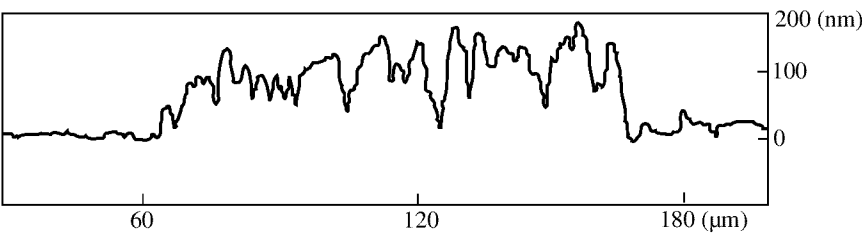
in the solution (Fig. 1(a)). (ii) Reaction between pairs of hydrazine admolecules can leave on the surface the nitrogen adatoms themselves (Fig. 1(b)) or with NH-bridge groups on the top (Fig. 1(c)), and correspondingly free  $\text{N}_2\text{H}_4$  or  $\text{NH}_3$  in the solutions.

For nitride treatment of GaAs wafers we used hydrazine-water solutions in the concentration range 3–10 M. We added small amounts of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  into the solutions to produce  $\text{SH}^-$  anions. It has been shown [3] that the interaction of the surface arsenic atoms with these anions leads to formation of the soluble thioarsenic acid and, hence, to uncovering of gallium layer. To prevent the interaction of surface gallium with  $\text{OH}^-$  anions [3] we advisedly decreased pH of the solutions till values 9–12 by adding  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ .

Chemical composition of the nitridized GaAs surfaces was analysed by X-ray photoelectron spectroscopy (XPS). These experiments were done in Japan Advanced Institute of Science and Technology (Ishikawa).

For excitation of the electron emission monochromatic  $\text{AlK}\alpha$  radiation was used. All spectra were observed at the photoelectron take-off angle of  $35^\circ$ . Figure 2 shows obtained XPS spectra. Both As(3d) and Ga(3d) core level spectra clearly demonstrate a presence of the components shifted to high binding energy (BE). Comparison of these spectra with those obtained for oxidized GaAs surface [4] allows to conclude that for Ga(3d) line chemically shifted component is due to Ga-N bonds. This conclusion is directly confirmed by observation of the line at  $\text{BE} = 397 \text{ eV}$  corresponding to emission from 1s level of nitrogen. The peak at  $\text{BE} = 392 \text{ eV}$  is attributed with gallium LMM Auger signal. For As(3d) line the shifted component occurs to be due to As-O bonds. We are speculating that this signal originates from oxidized molecules of thioarsenic acid physisorbed on the surface. Thus we conclude that the proposed chemical treatment, indeed, provides nitridation of the GaAs(100) surface through formation of Ga-N surface bonds.

We found that the nitrogen chemisorbed layer is chemically stable and can serve as a surface mask. Figure 3 shows a profile of (100)GaAs surface after selective (through windows in  $\text{SiO}_2$  mask) chemical nitridation and successive treatment in HF and  $\text{HCl}-\text{K}_2\text{Cr}_2\text{O}_7$  solutions. The nitridized area is seen as the elevated terrace over the etched substrate. This experiment confirms that the chemisorbed nitrogen atoms form a continuous nitride film



**Fig. 3.** Profile of chemically nitridized stripe on (100) GaAs after etching.

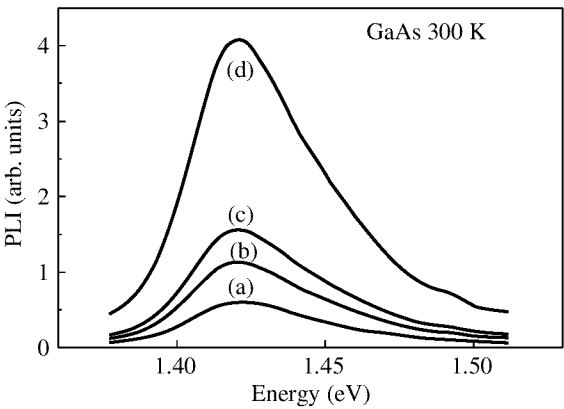
and therefore produce an effective surface chemical passivation.

To demonstrate the effect of electronic passivation, we studied behaviour of the RT photoluminescence of the nitridized n-GaAs samples taking as a reference the pieces of the same wafer passivated in  $\text{Na}_2\text{S}$  and  $(\text{NH}_4)_2\text{S}$ -water solutions. Figure 4 shows the PL spectra of (a) non-treated sample, (b) 1M sodium sulfide, and (c) 3M-ammonium sulfide-passivated samples, (d) chemically nitridized sample. Both sulfide treatments lead to an increasing the photoluminescence intensity (PLI) by a factor of 3–4. However, nitride-passivation produces a stronger PLI increase, by a factor of 7. This analysis unambiguously shows that the hydrazine solutions more efficiently reduce surface recombination velocity than the sodium sulfide and the ammonium sulfide ones.

The chemical stability in air of the nitrogen-passivated surfaces occur to be drastically stronger than of the sulfide-passivated ones. Indeed, we found that in the absence of the external light excitation, nitride passivated surfaces conserved their initial properties *during more than a month*.

*Acknowledgements*

This work was supported by the Russian Foundation for Basic Research (project No 99-02-18144) and partly supported by the Russian State Program “Surface Atomic Structures” (project No 3.7.99).



**Fig. 4.** Photoluminescence spectra of GaAs for untreated (100) surface (a), treated with  $\text{Na}_2\text{S}$  (b), with  $(\text{NH}_4)_2\text{S}$  (c), with hydrazine-based solution (d).

## References

- [1] H. D. Jung, N. Kumagai, T. Hanada, Z. Zhu, T. Yao, T. Yatsuda and K. Kimura, *J. Appl. Phys.* **83**, 5497 (1998).
- [2] I. Aksenov, Y. Nakada and H. Okimura, *J. Appl. Phys.* **84**, 3159 (1998).
- [3] V. P. Ulin, V. L. Berkovits, V. M. Lantratov and T. L. L'vova, *Proceedings of the 192th Meeting of the Electrochemical Society*, State of the Art Program on Compound Semiconductors XXVII, Paris, Sept. 1997 p. 343.
- [4] Akira Izumi, Atsushi Masuda and Hideki Matsumura, *Thin Solid Films*, (1999), (to be published).